Persistence of Bifenthrin in Sandy Loam Soil as Affected by Microbial Community

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Abstract Soil was fortified with bifenthrin at the level of 10 μg g⁻¹ soil. Soil samples were drawn at regular intervals of 0, 10, 20, 30 and 40 days. For extraction of bifenthrin, soil was extracted with acetone. Clean up was done by liquid-liquid partitioning with dichloromethane after diluting with brine solution. Quantification of bifenthrin residues was done by GC using mega bore column and ECD detector. Recovery of bifenthrin in soil ranged between 92.6 % and 93.8 % at 0.5 and 1.0 μ g g⁻¹. The instrumental limit of detection of bifenthrin was $0.005~\mu g~mL^{-1}$ and LOQ for soil by this method was found to be $0.05 \mu g g^{-1}$. The calibration curve was found to be linear within range the range of 0.01 and 0.10 $\mu g\ mL^{-1}$ concentration. The DT₅₀ (disappearance time for 50 % loss) of bifenthrin at the level of 10 μ g g⁻¹ in sterile and non sterile soil were found to be 330 and 147 days, respectively. A vast difference in the half life of sterile and non sterile soil indicated the presence of potential microbes for bifenthrin degradation.

Keywords Bifenthrin · Persistence · Residues · Sterile soil · Non sterile soil

Bifenthrin (2-Methyl-3-phenyl phenyl methyl (1*S*, 3*S*)-3-(Z)-2-chloro-3,3,3-triflouroprop-1-enyl 2,2-dimethylcy-clopropane-1-carboxylate; Fig. 1) is a third generation pyrethroid. It is used in agriculture, public health and forestry. It is an effective insecticide against stored grain pests and various insect pests of cotton, vegetables and fruit crops

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(Ali and Karim 1994; Chinniah and Ali 2000; Reddy and Rao 2002, Gupta et al. 2009). It has also been found effective against termites and ants through soil application. It has been used in public health programmes for control of mosquitoes (Mittal et al. 2002; Yadav et al. 2003). It has high toxicity to fish and other aquatic organisms. Bifenthrin has low potential to volatilize into air when applied to dry soil but somewhat higher potential when applied to wet soils. Thus it may be found in air attached to soil particles. Also it has low water solubility but correspondingly strong tendency to bind to soil therefore found in runoff sediments (Gan et al. 2005). Suspended soil particles contaminated with bifenthrin can increase the toxic concentration in water bodies. Different studies are available on microbial degradation of bifenthrin (Lee et al. 2004; Chen et al. 2012). The present study was undertaken to determine the persistence of bifenthrin in sterile and non sterile soil in order to assess the contribution of microbial community for bifenthrin degradation.

Materials and Methods

Bifenthrin technical grade (97.6 %) was used and stock solution of bifenthrin 1,000 μg mL⁻¹ was prepared in acetone. It was further, diluted to 100, 10, 5, 2, 1.0, 0.5, 0.1, 0.05 and 0.01 μg mL⁻¹ in hexane by serial dilution to determine the limit of detection of the instrument (IDL) and for analysis. The soil (0-15 cm) was collected from the farms of I.A.R.I., New Delhi for this study. Collected sample were air dried, finely ground using pestle-mortar then passed through 2 mm sieve. The soil was sandy loam soil with pH – 8.2 and organic carbon content – 0.4 %. One hundred gram soil sample was fortified with bifenthrin at the level of 1 and 0.05 μg g⁻¹ using appropriate standard bifenthrin solution for recovery studies in triplicate.

Fig. 1 Chemical structure of bifenthrin

A control soil sample was also maintained for each sampling by adding equal amount of acetone. Soil samples were extracted with 100 mL of acetone by shaking on mechanical horizontal shaker for 20 min. The extract was filtered through Buchner funnel, repeated twice using 50 and 30 mL acetone subsequently. Combined filtrate was concentrated on rotary vacuum evaporator. The residual extract was diluted with 120 mL of 10 % NaCl and partitioned with dichloromethane thrice (70 + 50 + 30 mL). Final extract was passed through anhydrous Na₂SO₄ (10–15 g) and solvent was evaporated to dryness. Residues were dissolved in hexane for GC- analysis. Shimadzu 17A Gas Chromatograph equipped with electron capture detector (ECD - Ni 63) and OV-5 mega bore column $(25 \text{ mm} \times 0.53 \text{ mm id})$ was used. The oven, injector and detector temperature were maintained at 240°C, 270°C and 300°C, respectively. Nitrogen was used as a carrier gas with flow rate of 20 mL min⁻¹. An aliquot of 3 μL of the standard bifenthrin solution and samples was injected and the retention time of bifenthrin was found to be 2.4 min.

Forty Erlenmeyer flasks containing 25 g of soil in each were taken for the persistence experiment. Twenty flasks were properly cotton plugged and sterilized by autoclaving in an autoclave for 20 min at 121°C and 15 psi consecutively for 3 times at an interval of 5 days. Bifenthrin was added at the level of 10 µg g⁻¹ in 15 flasks containing soil under laminar flow for sterile soil. For non sterile soil, bifenthrin was added under normal environmental condition in rest of 15 flasks. Five samples each of sterile and non sterile soil were kept as control. The moisture content of the soil was maintained by the addition of 1 mL of sterile distilled water every day for sterile soil. Moisture content of the non sterile soil was also maintained. All the soil samples were incubated at 28 ± 1 °C in the BOD incubator. At each sampling day (0,10,20,30 and 40 day) three treatments and one control from sterile and non sterile set of soil was drawn, extracted as mentioned above and bifenthrin content in each was analysed by GC.

Results and Discussion

Recoveries of bifenthrin from soil fortified at 1.0 and 0.05 $\mu g g^{-1}$ levels ranged between 92.6 % and 93.8 % (Table 1). LOD of the instrument was identified by signal

Table 1 Recovery of bifenthrin in soil of different concentration

Fortification Level (µg g ⁻¹)	Amount added (µg)	*Recovered amount $(\mu g \ g^{-1} \pm SD)$	Recovery (%)
1.0	100	93.8 ± 2.05	93.8
0.05	5.0	4.63 ± 0.074	92.6

^{*} Average of three replicates; SD standard deviation

Table 2 Residues of bifenthrin in sterile and non-sterile soil

Days after treatment	Residue*($\mu g g^{-1}$) $\pm SD$		
	Non–sterile soil (10 μg g ⁻¹)	Sterile soil (10 µg g ⁻¹)	
0	$10.09 \pm 0.007 (0)$	$10.05 \pm 0.006 (0)$	
10	$9.88 \pm 0.021 \; (2.08)$	$9.95 \pm 0.019 (0.5)$	
20	$9.43 \pm 0.043 (6.5)$	$9.86 \pm 0.014 (1.4)$	
30	$9.22 \pm 0.009 (8.67)$	9.73 ± 0.004 (2.7)	
40	$8.63 \pm 0.007 (14.5)$	9.33 ± 0.006 (6.7)	

^{*} Average of three replicates; Number within parenthesis indicate % dissipation

to noise ratio (3:1) by injecting lower concentration of bifenthrin solution serially. The calibration curve was found to be linear within the range of 0.01– $10~\mu g$ mL $^{-1}$ concentration with R^2 value of 0.988. The limit of detection (LOD) of bifenthrin was found to be 0.005 μg mL $^{-1}$ and LOQ for soil by this method was 0.05 μg g $^{-1}$. Initially bifenthrin residues in both sterile and non sterile soil were almost same (Table 2). On 10th day the residues in non sterile was found to be 9.88 μg g $^{-1}$ amounting 2 % dissipation as compared to sterile soil where only 0.5 % of bifenthrin dissipated. The decline in bifenthrin residues in non sterile was almost triple than the sterile soil on 20th and 30th day. On 40th day, the dissipation of bifenthrin in sterile and non-sterile soil was 6.7 % and 14.5 % respectively indicating the possible role of soil microorganisms.

The persistence of pesticides in soil are influenced by many factors such as the rate of application and moisture regime of bifenthrin in the soil (Manoj and Gajbhiye 2008), pH and temperature (Gupta and Gajbhiye 2008). Soil microbial community also has a significant role in the degradation of pesticides (Roy and Singh 2006, Singh et al. 2007, Maisnam et al. 2009). Bifenthrin dissipated steadily in both the soil however faster dissipation was found in non sterile soil compared to sterile soil (Table 2).

On 40th day $9.33 \,\mu g \, g^{-1}$ residue of bifenthrin was detected in sterile soil however in non-sterile soil it got reduced to $8.63 \,\mu g \, g^{-1}$. The dissipation of bifenthrin followed first order kinetics (Fig. 2). It has been shown that field dissipation half life for bifenthrin in a wide range of soils and conditions have been found to vary a lot. The half-life values in sterile and non sterile soil were found to



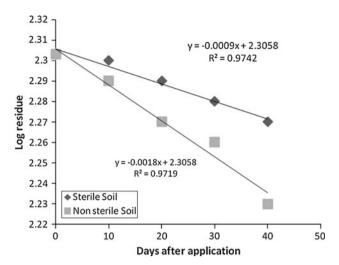


Fig. 2 First order dissipation kinetics of bifenthrin in sterile and non sterile soil

be 330 and 147 days, respectively. Reports also say that half-life of bifenthrin varies from 122 to 345 days (FMC 50429-025 1983). Lower values could be from the field studies where besides microbial factor other abiotic factors are also affecting the persistence of bifenthrin. The regression equations of bifenthrin in sterile and non sterile soil were Y = -0.0009x + 2.3058 with R^2 value of 0.9742 and Y = -0.0018x + 2.3058 with R^2 value of 0.9719 respectively.

As all the other parameters in sterile and non sterile soil were same, the difference in half life indicates that the microorganisms play an important role in the degradation of bifenthrin in soil. Bifenthrin is reported to be strongly adsorbed to soil so this could result in less availability of bifenthrin for microbial degradation. But a vast difference of half life in sterile and non sterile soil under study is a positive indication for potential microbial degradation of this persistent insecticide. The identification of potential microbes from this soil can be useful in remediation of bifenthrin contaminated soil environment and water bodies.

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